To:

#### From the INTERNATIONAL BUREAU

#### PCT

#### NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

BERGGREN OY AB
P.O. Box 16 Berggren Oy Mb
FIN-00101 Helsinki
FINLANDE 18 -10- 2000

O9 October 2000 (09.10.00)				
Applicant's or agent's file reference 50137	IMPORTANT NOTIFICATION			
International application No. PCT/FI00/00532	International filing date (day/month/year) 14 June 2000 (14.06.00)			
International publication date (day/month/year)  Not yet published	Priority date (day/month/year) 15 June 1999 (15.06.99)			
Applicant KEMIRA CHEMICALS OY et al				

- 1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterick appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- 2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- 3. An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- 4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date Priority application No. Country or regional Office of PCT receiving Office of PCT receiving Office

15 June 1999 (15.06.99) 991366 FI 28 Augu 2000 (28.08.00)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Authorized officer

Somsak Thiphrakesone

Telephone No. (41-22) 338.83.38

Facsimile No. (41-22) 740.14.35

#### A. CLASSIFICATION OF SUBJECT MATTER IPC7: D21H 21/14 // D21H 17:14 According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC7: D21H, D21C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched SE,DK,FI,NO classes as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. 1-10 US 5693185 A (HOU-MIN CHANG ET AL), X 2 December 1997 (02.12.97), column 1, line 61 - line 64, claims 1-5 WO 9722749 A1 (KVAERNER HYMAC INC.), 26 June 1997 1-10 X (26.06.97), see especially example 6, page 15, lines 10-12 and 31-34 1-8 GB 1119546 A (THE INSTITUTE OF PAPER CHEMISTRY), X 10 July 1968 (10.07.68), see claim 1 9-10 A Further documents are listed in the continuation of Box C. See patent family annex. later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention Special categories of cited documents "A" document defirming the general state of the art which is not considered to be of particular relevance "X" document of particular relevances the claimed invention cannot be "E" other document but published on or after the international filing date considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other "Y" document of particular relevance: the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other being obvious to a person skilled in the art comment published prior to the international filling date but later than the priority date claimed "&" document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 22 -09- 2000 15 Sept 2000 Authorized officer Name and mailing address of the ISA. Swedish Patent Office Marie Karlsson/Els Box 5055, S-102 42 STOCKHCLM

Telephone No. + 46 8 782 25 00

Facsimile No. +46 8 666 02 86



International application No. PCT/FI 00/00532

Patent document cited in search report			Publication date	F	Patent family member(s)	Publication date	
US	5693185	A	02/12/97	AU AU BR CA EP FI NO NZ US	672654 B 5347894 A 9307066 A 2141807 A 0660895 A 951334 A 951039 A 257205 A 5589032 A 9406964 A	10/10/96 12/04/94 13/10/99 31/03/94 05/07/95 21/03/95 17/03/95 28/10/96 31/12/96 31/03/94	
WO	9722749	A1	26/06/97	AU	4271596 A	14/07/97	
èв	1119546	A .	10/07/68	DE FI JP	1692855 A 48366 B 54017041 B	21/10/71 31/05/74 27/06/79	

## From the INTERNATIONAL BUREAU

#### **PCT**

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:
BERGGREN OY AB
P.O. Box 16
FIN-00101 Helsinki
FINLANDE
Gerraren Oy Ab

0 2 -01- 2001

JS/BE

Date of mailing (day/month/year)

21 December 2000 (21.12.00)

Applicant's or agent's file reference

50137

IMPORTANT NOTICE

International application No. PCT/FI00/00532

International filing date (day/month/year) 14 June 2000 (14.06.00) Priority date (day/month/year) 15 June 1999 (15.06.99)

Applicant

KEMIRA CHEMICALS OY et al

 Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice: AG.AU.DZ.KP.KR,MZ,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW. The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 21 December 2000 (21.12.00) under No. WO 00/77301

#### REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

#### REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Authorized officer

J. Zahra

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3722749



### From the INTERNATIONAL BUREAU

#### **PCT**

#### **NOTIFICATION OF ELECTION**

(PCT Rule 61.2)

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Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202

Date of mailing (day/month/year) 23 February 2001 (23.02.01)	ETATS-UNIS D'AMERIQUE in its capacity as elected Office		
International application No. PCT/FI00/00532	Applicant's or agent's file reference 50137		
International filing date (day/month/year) 14 June 2000 (14.06.00)	Priority date (day/month/year) 15 June 1999 (15.06.99)		
Applicant JÄKÄRÄ, Jukka et al			

	JAKATA, JUKKO ET UT
1.	The designated Office is hereby notified of its election made:  X in the demand filed with the International Preliminary Examining Authority on:
ŀ	23 December 2000 (23.12.00)
1	
	in a notice effecting later election filed with the International Bureau on:
2.	The election X was was not
	made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under
	Rule 32.2(b).
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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Authorized officer

F. Baechler

Telephone No.: (41-22) 338.83.38

Facsimile No.: (41-22) 740.14.35



From the: INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY To: SVENSSON, Johan BERGGREN OY AB P.O. Box 16 WRITTEN OPINION FIN-00101 Helsinki **FINLANDE** (PCT Rule 66) Date of mailing 10.04.2001 (day/month/year) within 3 month(s) **REPLY DUE** Applicant's or agent's file reference from the above date of mailing 50137/JS/BK Priority date (day/month/year) International filing date (day/month/year) International application No. 14/06/2000 15/06/1999 PCT/FI00/00532 International Patent Classification (IPC) or both national classification and IPC D21H21/14 Applicant KEMIRA CHEMICALS OY et al. This written opinion is the first drawn up by this International Preliminary Examining Authority. This opinion contains indications relating to the following items: Basis of the opinion ☐ Priority П □ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability Ш ☐ Lack of unity of invention IV Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement Certain document cited VΙ  $\boxtimes$ Certain defects in the international application VII Certain observations on the international application VIII The applicant is hereby invited to reply to this opinion. See the time limit indicated above. The applicant may, before the expiration of that time limit, When? request this Authority to grant an extension, see Rule 66.2(d). By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. How? For the form and the language of the amendments, see Rules 66.8 and 66.9. For an additional opportunity to submit amendments, see Rule 66.4. Also: For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6. If no reply is filed, the international preliminary examination report will be established on the basis of this opinion. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 15/10/2001.

Name and mailing address of the international preliminary examining authority:



European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 Authorized officer / Examiner

Jochheim, J

Formalities officer (incl. extension of time limits)

Ipinazar, P

Telephone No. +49 89 2399 8131



## WRITTEN OPINION

I. Basis	of the	opin	ion
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•									
1.	With regard to the <b>elements</b> of the international application (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"):								
	Description, pages:								
	1-6		as originally filed						
	Clai	ms, No.:							
	1-10	)	as originally filed						
	Dra	wings, sheets:							
	1/1		as originally filed						
2.	With lang	n regard to the <b>lan</b> q juage in which the	guage, all the elements marked above were available or furnished to this Authority in the international application was filed, unless otherwise indicated under this item.						
	These elements were available or furnished to this Authority in the following language: , which is:								
		the language of a	translation furnished for the purposes of the international search (under Rule 23.1(b)).						
		the language of p	ublication of the international application (under Rule 48.3(b)).						
		the language of a 55.2 and/or 55.3).	translation furnished for the purposes of international preliminary examination (under Rule						
3.	With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:								
		contained in the ir	nternational application in written form.						
		filed together with	the international application in computer readable form.						
		furnished subsequ	uently to this Authority in written form.						
		furnished subsequ	uently to this Authority in computer readable form.						
			at the subsequently furnished written sequence listing does not go beyond the disclosure in application as filed has been furnished.						
		The statement that listing has been for	at the information recorded in computer readable form is identical to the written sequence urnished.						
4.	The	amendments hav	e resulted in the cancellation of:						

pages:

Nos.:

☐ the description,

☐ the claims,

#### WRITTEN OPINION

International application No. PCT/FI00/00532

		the drawings,	sheets:
5.		•	n established as if (some of) the amendments had not been made, since they have been yond the disclosure as filed (Rule 70.2(c)):
		(Any replacement st report.)	neet containing such amendments must be referred to under item 1 and annexed to this
6.	Ado	ditional observations.	if necessary:

- V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Novelty (N)

Claims

1-9: Yes / 10: No

Inventive step (IS)

Claims 1-10: No

Industrial applicability (IA)

Claims

1-10: Yes

2. Citations and explanations see separate sheet

#### VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted: see separate sheet

#### VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made: see separate sheet

Reference is made to the following document/s/:

**D1**: US-A-5693185 **D2**: WO-A1-9722749 **D3**: GB-A-1119546

#### Re Item V

Reasoned statement under Rule 66.2(a)(ii) PCT with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- Claim 10 does not fulfill Article 33(2) PCT because this claim is interpreted in 1. the manner: Paper, obtainable from pulp treated according to claim 1. Such a paper is also obtainable by other methods, as shown in D3, example 1 (values of achieved brightness and opacity similar to those of example 2 of the present application).
- The subject-matter of claim 1 consists in the selection of an amount of 0.5 5 2. kg/ton of pulp of per-carboxylic acid from the range of up to 25 kg/ton of pulp described in the applicants citation (Tappi publication, Vol. 48, No. 2 (2/1965), W. H. Rapson et al. Paper Bleaching-A New Process, pp. 65-72). Such a selection can only be regarded as inventive, if the chosen range presents unexpected effects or properties in relation to the rest of the range. However, it is well known in the art (see for example Dence, C.W. et al., "Pulp Bleaching - Principles and Practice", 1st edn, Tappi Press, 1996, p 477) that bleaching is inversely related to the opacity of the pulp, i.e. that a high brightness due to strong bleaching results in low opacity. Therefore, the selection made in claim 1 is considered to be obvious to a person skilled in the art in order to arrive at the solution of the problem posed which could be regarded as providing a method to keep opacity of mechanical pulp at a maximum with percarboxylic acids. The solution proposed in claim 1 of the present application can therefore not be considered as involving an inventive step (Article 33(3) PCT).
- A similar argumentation as in V.4 applies to claim 9: D2, which is considered to be 3. the closest state of the art, teaches the use of a combination of Caro's acid and

peracetic acid to improve optical properties of pulp (example 6). In table 10 of D2 it is shown that the use of such a combination of acids results in higher opacity of the pulp as compared to untreated pulp. The selection made in claim 9 can only be regarded as being inventive if the selection presents unexpected effects or properties in relation to the rest of the range. However, such an effect or property can not be seen since the applicant fails to provide an example in which pulp is bleached with peracetic acid alone.

- Dependent claims 2-8 do not contain any features which, in combination with 4. the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step (Article 33(3) PCT), the reasons being as follows:
- In claims 2, 4 optimisations of the method of claim 1 are defined which come 4.1 within the scope of the customary practice followed by persons skilled in the art, especially as the advantages thus achieved can readily be foreseen. Consequently, the subject-matter of claims 2 and 4 also lacks an inventive step.
- 4.2 Claim 3: The selection of performic acid, peracetic acid or perpropionic acid as percarboxylic acid is merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed.
- 4.3 The additional subject-matter of claim 5 is disclosed by D1 (column 1, lines 15-19) and is therefore **not inventive** either.
- 4.4 The additional subject-matter of claim 6 is disclosed by D2 (example 5) and is therefore not inventive either.
- 4.5 The additional subject-matter of claim 7 is disclosed by D1 (column 1, lines 15-19) and is therefore **not inventive** either.
- 4.6 The requirements for industrial applicability according to Article 33(4) PCT appear to be fulfilled.

#### Re Item VII

#### Certain defects in the international application

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art 1. disclosed in the documents D1-D3 is not mentioned in the description, nor are these documents identified therein.

#### Re Item VIII

#### Certain observations on the international application

It is unclear which methods have been employed to measure the opacity in the 1. given examples of the present application. Therefore, meaningful comparison with prior art (in particular D2 and D3) is limited to the assumption that similar methods have been used by the applicant.

#### **Further Remarks**

Upon amending, the applicant is expected to provide a full text translation of 1. JP 57-21591 so that the pertinence of that prior art can be fully assesed.



## From the INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SVENSSON, Johan BERGGREN OY AB P.O. Box 16 FIN-00101 Helsinki FINLANDE

i Bergyren Oy Ab 29-08-2001 PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing

(day/month/year)

27.08.2001

Applicant's or agent's file reference

International application No.

50137/JS/BK

PCT/FI00/00532

International filing date (day/month/year)

14/06/2000

Priority date (day/month/year)

IMPORTANT NOTIFICATION

15/06/1999

Applicant

KEMIRA CHEMICALS OY et al.

- 1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
- 2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- 3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

#### 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

European Patent Office D-80298 Munich

Tel. +49 89 2399 - 0 Tx: 523656 epmu d

Fax: +49 89 2399 - 4465

Authorized officer Fuerbass, C

Tel.+49 89 2399-8132





# **PCT**

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

.,	or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
50137/JS	/BK		
	application No.	International filing date (day/mo	
PCT/FI00		14/06/2000	15/06/1999
Internationa D21H21/		or national classification and IPC	
Applicant			
KEMIRA	CHEMICALS OY et a	l <u>-</u>	
1. This ir and is	nternational preliminary transmitted to the appli	examination report has been prepa cant according to Article 36.	ared by this International Preliminary Examining Authority
2. This F	REPORT consists of a to	otal of 5 sheets, including this cove	er sheet.
be	een amended and are the	panied by ANNEXES, i.e. sheets one basis for this report and/or sheetion 607 of the Administrative Instru	If the description, claims and/or drawings which have ts containing rectifications made before this Authority actions under the PCT).
Those	annexes consist of a to	otal of 1 sheets	
mese	differes consist of a to	Adi Oi 1 Sheets.	
	_	ns relating to the following items:	
1	<ul><li>☑ Basis of the repo</li><li>☑ Priority</li></ul>		
1  11		nt of opinion with regard to novelty	, inventive step and industrial applicability
IV	☐ Lack of unity of ir		, intolling clop and industrial approximation,
V	☑ Reasoned statem		to novelty, inventive step or industrial applicability;
VI	☐ Certain docume	nts cited	
VII	☐ Certain defects in	the international application	
VIII	☐ Certain observati	ons on the international application	1
Date of sub	mission of the demand	Date	e of completion of this report
23/12/20	00	27.0	08.2001
Name and	mailing address of the inter	national Auti	horized officer
	examining authority:		STATE OF THE PROPERTY OF THE P
<u></u>	European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx:		chheim, J
	Fax: +49 89 2399 - 4465	1	ephone No. +49 89 2399 8632



International application No. PCT/FI00/00532

#### I. Basis of the report

the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)):  Description, pages:							s "originally file	ario ed"	
	1-6		as originally filed						
	Clai	ms, No.:							
	1-9		as received on	02/07/200	1	with letter of	29/	06/2001	
	Drav	wings, sheets:							
	1/1		as originally filed						
2.	With lang	regard to the <b>lan</b> quage in which the	guage, all the elements international application	marked above were was filed, unless o	e a	vailable or furnis erwise indicated (	ned to this under this	s Authority in t	he
	The	se elements were	available or furnished to	this Authority in the	e fo	ollowing language	∍: , whic	ch is:	
		the language of a	translation furnished for	the purposes of th	e ii	nternational sear	ch (under	Rule 23.1(b))	
		the language of p	ublication of the internat	ional application (u	nde	er Rule 48.3(b)).			
		the language of a 55.2 and/or 55.3).	translation furnished for	the purposes of in	ter	national prelimina	ary exami	nation (under	Rule
3.	With inter	n regard to any <b>nu</b> rnational prelimina	cleotide and/or amino a ry examination was carr	acid sequence disc ied out on the basis	clo s o	sed in the interna f the sequence lis	ıtional apı sting:	plication, the	
		contained in the in	ntemational application i	n written form.					
		filed together with	the international applica	ation in computer re	ead	lable form.			
		furnished subseq	uently to this Authority in	written form.					
		•	uently to this Authority in						
		the international a	at the subsequently furni application as filed has b	een furnished.					
		The statement that listing has been for	at the information record urnished.	ed in computer rea	da	ble form is identi	cal to the	written sequer	nce
4.	The	amendments hav	re resulted in the cancell	ation of:					
		the description,	pages:						
		the claims,	Nos.:						

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/FI00/00532

		the drawings,	sheets:		
5.					ome of) the ame <b>nd</b> ments had not been made, since they have beer as filed (Rule 70.2(c)):
		(Any replacement she report.)	et contail	ning such	amendments must be referred to under item 1 and annexed to this
6.	Add	itional observations, if	necessar	y:	
V.		soned statement und tions and explanation			ith regard to novelty, inventive step or industrial applicability; the statement
1.	Stat	rement			
	Nov	relty (N)	Yes: No:	Claims Claims	1-9
	Inve	entive step (IS)	Yes: No:	Claims Claims	1-9
		ustrial applicability (IA)			1-9

2. Citations and explanations see separate sheet

#### Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

**D1**: US-A-5693185 **D2**: WO-A1-9722749 **D3**: GB-A-1119546

1. Content of the application

The subject-matter of independent claim 1 relates to a method for treating mechanical pulp, comprising the addition of an aliphatic carboxylic acid to the pulp in the amount of 0,5 - 5 kg/ton of pulp.

2. Summary of prior art and novelty

**Document D1** discloses a process for treating a substrate, e.g., lignocellulosic pulp or cellulosic pulps, with a mixed peracid solution comprising percarboxylic acid and Caro's acid (in the amount of 1% equivalent of H2O2 based on pulp) which results in a higher conversion rate of the active oxygen in the hydrogen peroxide in order to provide an inexpensive and effective delignification and/or bleaching solution and the process for making the mixed peracid solution.

Claim 1 differs at least in that the amount of aliphatic carboxylic acid used is smaller than 1% based on pulp, namely at maximum 0,5 % or 5 kg/ton of pulp. The same feature also establishes novelty over documents **D2** and **D3**. Therefore, the subject-matter of claim 1 and claims 2-9, which are dependent on claim 1, is novel over **D1-D3** and fulfills Article 33(2) PCT.

3.1 The closest prior art is seen in document **D2** because it relates to a process of pre-treatment of lignocellulosic materials with (among others) a mixture of Caro's acid and peracetic acid so as to render the fibers flexible and conformable with low refining energy while improving the strength and brightness of the resulting

pulp and subsequently subjecting the fibers to refining.

- 3.2 The **objective problem** of the present application can be formulated as: to provide a **method** of improving the opacity of mechanical pulp while the brightness of the pulp remains unchanged.
- 3.3 None of the documents **D1-D3**, or a combination of any two, teaches or fairly suggests to the person skilled in the art to use a <u>small amount</u> (i.e. at maximum 0,5 weight percent per ton of pulp) of an aliphatic percarboxylic acid of claim 1 for improving the opacity of mechanical pulp while <u>the brightness of the pulp remains unchanged</u> as shown by the applicant in examples 1 and 2. The effect is in deed surprising, because the teaching of text books well known in the art (for example Dence, C.W. et al., "Pulp Bleaching Principles and Practice", 1st edn, Tappi Press, 1996, p 477) suggests that bleaching is inversely related to the opacity of the pulp, i.e. that a high brightness due to strong bleaching results in low opacity. The skilled person would therefore assume that the use of a bleaching agent (like the aliphatic percarboxylic acid of claim 1) would cause the pulp to loose opacity and he would not arrive at the solution of the problem of the invention.

Therefore, it is concluded that claims 1-9 are inventive and fulfill Article 33(3) PCT.

4. The requirements for industrial applicability according to Article 33(4) are fulfilled.

# **PCT**

DECID 29 AUG 2091

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's	or age	nt's file reference	Saa No	tification of Transmittal of International
50137/JS/BK			FOR FURTHER ACTION Prelimin	nary Examination Report (Form PCT/IPEA/416)
			International filing date (day/month/year)	Priority date (day/month/year)
PCT/FI0	• •		14/06/2000	15/06/1999
			tional classification and IPC	
D21H21		,		
Applicant				
KEMIRA	CHE	MICALS OY et al.		
			in ation report has been prepared by this	International Preliminary Examining Authority
1. This and i	interna s trans	ational preliminary exam smitted to the applicant a	according to Article 36.	miteriational Frommitary Examining Court,
2. This	REPO	RT consists of a total of	5 sheets, including this cover sheet.	
				ration, cloims and/or drawings which have
	neen a	mended and are the bas	sis for this report and/or sheets containin	ption, claims and/or drawings which have g rectifications made before this Authority
	see R	ule 70.16 and Section 6	07 of the Administrative Instructions unde	er the PCT).
Thes	e ann	exes consist of a total of	1 sheets.	
11100	oc arm			
3. This	report	contains indications rela	ating to the following items:	
,	$\boxtimes$	Basis of the report		
11		Priority		
111			opinion with regard to novelty, inventive s	step and industrial applicability
١٧		Lack of unity of inventi	on	
V	Ø	Reasoned statement u citations and explanati	inder Article 35(2) with regard to novelty, ions suporting such statement	inventive step or industrial applicability;
VI		Certain documents cit		
VII			international application	
VIII		Certain observations of	on the international application	
Date of su	issimdu	on of the demand	Date of completion	on of this report
00/40/0	000		27.08.2001	
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	<b>)</b> D-8	0298 Munich	Jochheim, J	
Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465			· · · · · · · · · · · · · · · · · · ·	149 89 2399 8632



## INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/FI00/00532

I. Bas	is of	the	report
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1.	the I	receiving Office in	ments of the internationaresponse to an invitation of this report since they o	n under Article 14 are	reterred to in this	ich have been furnished to report as "originally filed" 16 and 70.17)):
	1-6		as originally filed			
	Clai	ms, No.:				
	1-9		as received on	02/07/2001	with letter of	29/06/2001
	Dra	wings, sheets:				
	1/1		as originally filed			
2.	With lang	n regard to the <b>lan</b> guage in which the	guage, all the elements international application	marked above were an was filed, unless oth	available or furnis erwise indicated	hed to this Authority in the under this item.
	The	se elements were	available or furnished to	o this Authority in the f	following languag	e: , which is:
		the language of a	translation furnished fo	or the purposes of the	international sear	ch (under Rule 23.1(b)).
			oublication of the interna			
		the language of a 55.2 and/or 55.3)	a translation furnished fo	or the purposes of inte	rnational prelimin	ary examination (under Rule
3.	Witl inte	n regard to any <b>nu</b> rnational prelimina	icleotide and/or amino ary examination was car	acid sequence discleried out on the basis	osed in the internant of the sequence li	ational application, the sting:
		contained in the i	international application	in written form.		
		filed together with	n the international applic	cation in computer rea	dable form.	
		furnished subseq	quently to this Authority i	in written form.		
			quently to this Authority i			
		the international	application as filed has	been furnished.		t go beyond the disclosure in
		The statement th		ded in computer reada	able form is identi	cal to the written sequence
4	. The	e amendments hav	ve resulted in the cance	llation of:		
		the description,	pages:			
		the claims,	Nos.:			



## INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/FI00/00532

		the drawings,	sheets:				
5.	.   This report has been established as if (some of) the amendments had not been made, since they have bee considered to go beyond the disclosure as filed (Rule 70.2(c)):						
		(Any replacement she report.)	eet contain	ing such	amendments must be referred to under item 1 and annexed to this		
6.	Ado	ditional observations, if	f necessary	<b>/</b> :			
V.	Rea cita	asoned statement un ations and explanatio	der Article ons suppoi	e 35(2) wi rting suc	ith regard to novelty, inventive step or industrial applicability; h statement		
1.	Sta	tement					
	Nov	velty (N)	Yes: No:	Claims Claims	1-9		
	Inv	entive step (IS)	Yes: No:	Claims Claims	1-9		
	Ind	ustrial applicability (IA)	) Yes: No:	Claims Claims	1-9		

2. Citations and explanations see separate sheet

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## INTERNATIONAL PRELIMINARY **EXAMINATION REPORT - SEPARATE SHEET**



#### Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

**D1**: US-A-5693185 **D2**: WO-A1-9722749 D3: GB-A-1119546

Content of the application 1.

> The subject-matter of independent claim 1 relates to a method for treating mechanical pulp, comprising the addition of an aliphatic carboxylic acid to the pulp in the amount of 0,5 - 5 kg/ton of pulp.

Summary of prior art and novelty 2.

> Document D1 discloses a process for treating a substrate, e.g., lignocellulosic pulp or cellulosic pulps, with a mixed peracid solution comprising percarboxylic acid and Caro's acid (in the amount of 1% equivalent of H2O2 based on pulp) which results in a higher conversion rate of the active oxygen in the hydrogen peroxide in order to provide an inexpensive and effective delignification and/or bleaching solution and the process for making the mixed peracid solution.

Claim 1 differs at least in that the amount of aliphatic carboxylic acid used is smaller than 1% based on pulp, namely at maximum 0,5 % or 5 kg/ton of pulp. The same feature also establishes novelty over documents D2 and D3. Therefore, the subject-matter of claim 1 and claims 2-9, which are dependent on claim 1, is novel over D1-D3 and fulfills Article 33(2) PCT.

3.1 The closest prior art is seen in document D2 because it relates to a process of pre-treatment of lignocellulosic materials with (among others) a mixture of Caro's acid and peracetic acid so as to render the fibers flexible and conformable with low refining energy while improving the strength and brightness of the resulting

## INTERNATIONAL PRELIMINARY **EXAMINATION REPORT - SEPARATE SHEET**

pulp and subsequently subjecting the fibers to refining.

- 3.2 The objective problem of the present application can be formulated as: to provide a method of improving the opacity of mechanical pulp while the brightness of the pulp remains unchanged.
- 3.3 None of the documents D1-D3, or a combination of any two, teaches or fairly suggests to the person skilled in the art to use a small amount (i.e. at maximum 0,5 weight percent per ton of pulp) of an aliphatic percarboxylic acid of claim 1 for improving the opacity of mechanical pulp while the brightness of the pulp remains unchanged as shown by the applicant in examples 1 and 2. The effect is in deed surprising, because the teaching of text books well known in the art (for example Dence, C.W. et al., "Pulp Bleaching - Principles and Practice", 1st edn, Tappi Press, 1996, p 477) suggests that bleaching is inversely related to the opacity of the pulp, i.e. that a high brightness due to strong bleaching results in low opacity. The skilled person would therefore assume that the use of a bleaching agent (like the aliphatic percarboxylic acid of claim 1) would cause the pulp to loose opacity and he would not arrive at the solution of the problem of the invention.

Therefore, it is concluded that claims 1-9 are inventive and fulfill Article 33(3) PCT.

The requirements for industrial applicability according to Article 33(4) are fulfilled. 4.

#### Amended claims

- 1. A method for treating mechanical pulp, characterized in that an aliphatic percarboxylic acid is added to the pulp, in the amount of 0.5 5 kg/ton of pulp, to affect the opacity.
- 2. A method according to Claim 1, characterized in that the amount of aliphatic percarboxylic acid that is added is 1-3 kg/ton of pulp.
- 3. A method according to Claim 1 or 2, **characterized** in that the aliphatic percarboxylic acid is selected from among performic acid, peracetic acid or perpropionic acid.
- 4. A method according to any of the preceding Claims, characterized in that the aliphatic percarboxylic acid is distilled or equilibrated peracetic acid.
- 5. A method according to Claim 1, characterized in that the aliphatic percarboxylic acid is added to the pulp in connection with or after bleaching.
- 6. A method according to Claim 5, characterized in that the pulp has been bleached with hydrogen peroxide and/or dithionite.
- 7. A method according to Claim 1 or 5, characterized in that the aliphatic percarboxylic acid is typically added at a pulp consistency of 1-40%.
- 8. A method according to Claim 1, characterized in that a mixture of aliphatic percarboxylic acid and Caro's acid is added to the pulp.
- 9. The use of aliphatic percarboxylic acid to improve the opacity of mechanical pulp, in which the amount of percarboxylic acid is 0.5 5 kg/ton of pulp.

#### 1/4

# RECORD COPY

PCT REQUEST

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50137

0	For receiving Office use only	PCT/FI 0 0 / 0 0 5 3 2
0-1	International Application No.	PC1/F1 0 0 7 0 0 0 0 1
0-2	International Filing Date	1 4 JUN 2000 (1 4 -06- 2000)
0-3	Name of receiving Office and "PCT International Application"	The Finnish Patent Office PCT International Application
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.90 (updated 10.05.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	National Board of Patents and Registration (Finland) (RO/FI)
0-7	Applicant's or agent's file reference	50137
l	Title of invention	PROCESS FOR THE TREATMENT OF MECHANICAL PULPS
īi.	Applicant	
11-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
11-4	Name	KEMIRA CHEMICALS OY
II-5	Address:	P.O. Box 330 FIN-00101 Helsinki
		Finland
II-6	State of nationality	FI
11-7	State of residence	FI
111-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
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III-1-5	Address:	Koulukatu 32 A 10
		FIN-65100 Vaasa
		Finland
III-1-6	State of nationality	FI
111-1-7	State of residence	FI



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III-2	Applicant and/or inventor	
111-2-1	This person is:	applicant and inventor
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III-2-7	State of residence	FI
IV-1	Agent or common representative; or	
	address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
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IV-1-4	Facsimile No.	+358-9-6933944
IV-1-5	e-mail	email.box@berggren.fi
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT  EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT  EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT  OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW



#### **PCT REQUEST**

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V-5	Precautionary Designation Statement		
	In addition to the designations made		
	under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b)		
	all designations which would be		
	permitted under the PCT except any		
	designation(s) of the State(s) indicated		
	under item V-6 below. The applicant		
	declares that those additional		
	designations are subject to confirmation		
	and that any designation which is not		
	confirmed before the expiration of 15		
	months from the priority date is to be		
	regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary	NONE	
V-0	designations	NONE	
VI-1	Priority claim of earlier national		
•••	application		
VI-1-1	Filing date	15 June 1999 (15.06.	1999)
VI-1-2	Number	991366	
VI-1-3	Country	FI	
VI-2	Priority document request		
	The receiving Office is requested to	VI-1	
	prepare and transmit to the International		
	Bureau a certified copy of the earlier		
	application(s) identified above as		
VII-1	item(s): International Searching Authority	Swedish Patent Office	o /TCA/CE\
VII-1	Chosen	Swedish Patent Office	e (ISA/SE)
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	4	_
VIII-2	Description	6	
VIII-2 VIII-3	Description Claims	1	-
			- 50137.txt
VIII-3	Claims	1 1 1	-
VIII-3 VIII-4	Claims Abstract	1 1 1 13	- 50137.txt -
VIII-3 VIII-4 VIII-5	Claims Abstract Drawings TOTAL Accompanying items	1 1 1	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5	Claims Abstract Drawings TOTAL	1 1 1 13	- 50137.txt -
VIII-3 VIII-4 VIII-5 VIII-7	Claims Abstract Drawings TOTAL  Accompanying items Fee calculation sheet Copy of general power of attorney	1 1 1 1 paper document(s) attached	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet	1 1 1 13 paper document(s) attached	- 50137.txt - electronic file(s) attached -
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract	1 1 1 1 13 paper document(s) attached  ✓	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16 VIII-18	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract Language of filing of the international application	1 1 1 1 13 paper document(s) attached  ✓	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16	Claims  Abstract  Drawings  TOTAL  Accompanying items  Fee calculation sheet  Copy of general power of attorney  PCT-EASY diskette  Figure of the drawings which should accompany the abstract  Language of filing of the international	1 1 1 1 13 paper document(s) attached  ✓	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16 VIII-18	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract Language of filing of the international application	1 1 1 1 13 paper document(s) attached  ✓	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16 VIII-18 VIII-19 IX-1	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract Language of filing of the international application Signature of applicant or agent	1 1 1 13 paper document(s) attached    Finnish	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16 VIII-18 VIII-19 IX-1	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract Language of filing of the international application Signature of applicant or agent	1 1 1 13 paper document(s) attached  / - Finnish  BERGGREN OY AB	- 50137.txt - electronic file(s) attached
VIII-3 VIII-4 VIII-5 VIII-7 VIII-8 VIII-10 VIII-16 VIII-18 VIII-19 IX-1	Claims Abstract Drawings TOTAL Accompanying items Fee calculation sheet Copy of general power of attorney PCT-EASY diskette Figure of the drawings which should accompany the abstract Language of filing of the international application Signature of applicant or agent	1 1 1 13 paper document(s) attached    Finnish	- 50137.txt - electronic file(s) attached

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10-1	Date of actual receipt of the	1 4 JUN 2000	(1 4 -05- 2000)
	purported international application	1 1 3011 2000	





#### **PCT REQUEST**

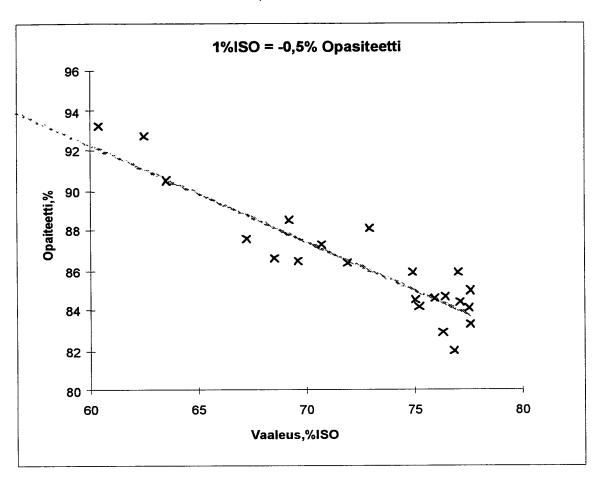
Original (for SUBMISSION) - printed on 14.06.2000 10:59:08 AM

50137

10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/SE
10-6	Transmittal of search copy delayed until search fee is paid	

#### FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by	ļ								(0.3.07.00)
	the International Bureau		ก :	3	1	11	[ '	V_	2000	( U 3, U/, UU /
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Kuva 1

#### Menetelmä mekaanisten massojen käsittelemiseksi

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Keksintö kohdistuu mekaanisten massojen käsittelymenetelmään, jolla voidaan vaikuttaa massan opasiteettiin.

5 Paperin läpikuultamattomuutta kuvaa opasiteetti, joka on vaaleuden ohella eräs tärkeä massan ominaisuus paperinvalmistuksessa. Lähes poikkeuksetta massan opasiteetti kuitenkin laskee vaaleuden noustessa. Nykyisin mekaanisia massoja (hierteet, hiokkeet ja kemimekaaniset massat) valkaistaan yhä useammin vetyperoksidilla. Myös ditioniittivalkaisua käytetään, joko yksin tai yhdessä peroksidivalkaisun kanssa, jolloin ditioniittia käytetään joko jauhinvalkaisuna tai jälkivalkaisuna. Massojen, 10 etenkin mekaanisten massojen, peroksidivalkaisussa opasiteetin lasku havaitaan selvästi, kun taas ditioniittivalkaisu ei välttämättä alenna opasiteettia. Yleensä massan opasiteetti laskee sitä enemmän, mitä vaaleammaksi massa valkaistaan. Tämä ilmenee oheisesta kuvasta 1, joka esittää kuusi-TMp:n opasiteetin muutosta valkaistaessa massaa peroksidilla eri vaaleustasoille. Tietyissä paperilaaduissa opasiteetti on tär-15 keä ominaisuus. Kun halutaan edistää peroksidivalkaisua ditioniittivalkaisun kustannuksella, olisi tärkeää pystyä optimoimaan peroksidivalkaisua niin, että opasiteetti säilyisi mahdollisimman korkeana vaaleuden kasvaessa.

Mekaanisten massojen peroksidivalkaisussa käytetyt kemikaalit ovat yleisemmin vetyperoksidi, lipeä (alkali) ja vesilasi. Emäksen tarkoituksena on nostaa pH riittävän korkealle, jotta vetyperoksidi dissosioituu tuottaen perhydroksyylianioneja. Vesilasin tarkoituksena on stabiloida vetyperoksidivalkaisua.

On tunnettua, että peretikkahappoa voidaan muodostaa in situ esimerkiksi asetanhydridistä tai TAED:sta (tetra-asetyyli-etyleeni-diamiini) tai jostakin muusta vastaavasta aktivaattorista. TAED:n haittana on sen korkea hinta ja se, että se on kiinteä aine. TAED jouduttaisiin dispergoimaan veteen ennen massaan lisäämistä, mikä tekee sen käytön hankalaksi. Lisäksi TAED sisältää typpeä, mikä voi tulla ongelmaksi ympäristön suojelun kannalta. Asetanhydridi olisi suhteellisen halpaa, mutta se aiheuttaisi hajuhaittoja ja olisi työsuojelun kannalta hankala aine. Lisäksi alkaliseen valkaisuliuokseen (NaOH + H<sub>2</sub>O<sub>2</sub> + vesilasi) syötettynä se aiheuttaisi helposti silikaattisaostumia ja kuluttaisi lipeää.

Papereiden valmistuksessa tähdätään yhä korkeampiin vaaleuksiin. Paperin vaaleuteen voidaan vaikuttaa esimerkiksi käsittelemällä paperia päällysteaineilla, jotka sisältävät mm. pigmenttejä, sideaineita ja pehmitinaineita (JP-hakemus 284598).

Kuitenkin useiden päällystysaineiden käyttö paperinvalmistuksen loppuvaiheessa lisää edelleen valmistuskustannuksia.

Teknisesti käyttökelpoisen massan opasiteettiin vaikuttavan aineen tulisi olla nestemäinen, pysyvä ja mieluiten pH-arvoltaan sopiva, jottei valkaisussa syntyisi sili-kaattisaostumia. Lisäetuna olisi typetön aine ympäristönsuojelullisista syistä. Valkaisun apuaineen tulee myös olla edullista paperinvalmistajille. Massojen valkaisuun on siis löydettävä aine, joka edellä mainittujen ehtojen täyttämiseksi on helposti saatavissa oleva kohtuuhintainen kaupallinen kemikaali ja joka voidaan lisätä jo massan valkaisuvaiheessa. Lisäksi on myös kiinnitettävä huomiota aineen muihin vaikutuksiin, kuten käyttökelpoisuuteen tehdasoloissa.

Tämän keksinnön tarkoituksena on löytää käyttökelpoinen massan valkaisussa käytettävä opasiteettiin vaikuttava aine, joka täyttää edellä mainitut vaatimukset.

Keksinnön pääasialliset tunnusmerkit ilmenevät oheisista patenttivaatimuksista.

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Nyt on yllättäen havaittu, että lisättäessä pieni annos perhappoa joko peroksidivalkaisuun tai peroksidivalkaisun jälkikäsittelynä massan opasiteetti paranee verrattuna pelkällä vetyperoksidilla valkaistuun vastaavan vaaleustason massaan. Samalla on havaittu, etteivät perhapot juurikaan nosta vaaleutta.

Peretikkahapon käyttö kemiallisten massojen valkaisuun on tunnettu esimerkiksi japanilaisesta hakemusjulkaisusta JP 57-21591. Tämän kaltaiset valkaisuprosessit tähtäävät kuitenkin ligniinin poistoon massasta, eikä tässä tapauksessa ole kyse minkäänlaisesta tarkoituksesta säätää massan opasiteettia.

Julkaisussa Tappi, Vol. 48, no.2 (2/1965), W.H. Rapson et al. Paper Bleaching - A New Process, s. 65-72 esitetään menetelmä paperin valkaisemiseksi käyttäen mm. peretikkahappoa. Tässä menetelmässä ei kuitenkaan tähdätä massan opasiteetin parantamiseen, vaan vaaleuden nostamiseen. Esitetyssä menetelmässä käytetään myös peretikkahappoa huomattavan suuria määriä, noin 1,2-2,5 % (eli 12-25 kg/massatonni). Tällainen annos voi liuottaa huomattavasti ligniiniä ym. massasta, jolloin paperinvalmistusprosessi voi vakavasti häiriintyä. Julkaisusta voidaan myös havaita menetelmän teknisen suoritustavan poikkeavan keksinnöstämme.

Perhappojen käyttö biosidina on myös tunnettu esimerkiksi julkaisusta Kemia, no. 3 (1995), Jyri Maunuksela, Mikrobien torjunta peretikkahapolla, s. 242-244. Tällainen menetelmä tähtää ainoastaan mikrobikasvustojen hävittämiseen paperikoneelta. On itsestään selvää, että tehokkaana biosidina tunnettu peretikkahappo estää mikrobi-

toiminnan vesikierroista, mikäli sitä on siellä riittävä määrä. Julkaisussa esitetyssä menetelmässä käytetään ns. tasapainoperetikkahappoa, joka sisältää huomattavan määrän vapaata etikkahappoa ja vetyperoksidia. Perhapon joukossa tuleva etikkahappo ja vetyperoksidi voivat haitata paperinvalmistusprosessia.

On esitetty myös perhappoon perustuvia valkaisumenetelmiä, joissa tavoitteena on ollut massan vaaleuden parantaminen normaaleihin valkaisumenetelmiin verrattuna. Tällainen menetelmä on esitetty esimerkiksi julkaisussa Pulp and Paper Magazine of Canada, Convention issue, 1972, s. 123-131 ja saman lehden numerossa 3/1968 sivuilla 51-60. Näissä menetelmissä käytettävät perhappoannokset ovat hyvin suuria ja näin ollen liuottavat huomattavasti ligniiniä kuitujen pinnoista. Lisäksi nämä menetelmät tähtäsivät massan vaaleuden nostamiseen eli valkaisuun.

Erona keksintöömme edellä mainituissa käsittelyissä on nimenomaan se, ettei niissä esitetyillä tavoilla toteutetuissa perhappokäsittelyissä onnistuttu nostamaan massan opasiteettia eikä opasiteetin merkittävää nousua missään edellä mainituissa julkaisuissa myöskään pyritty saamaan aikaan.

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Keksintö koskee menetelmää, jossa perhappo lisätään joko peroksidivalkaisuun tai edullisesti peroksidivalkaisun jälkeen joko valkaistun massan varastotorniin tai esimerkiksi paperikoneelle konemassan joukkoon. Perhappoa lisätään massaan tyypillisesti noin 1-3 kg/massatonni. Pienen annoksen vuoksi perhappo ei liuota ligniiniä tms. massasta, jolloin se ei myöskään häiritse paperinvalmistusprosessia. Erityisen edullista on käyttää perhappoliuoksia, jotka on puhdistettu niin, että ne sisältävät lähinnä vain ko. perhappoa ja vettä. Tällöin perhapon lisäys ei vaikuta merkittävästi massasulpun pH-arvoon, eikä prosessiin tule ylimääräistä COD:ta. Tunnetuista perhappoihin perustuvista menetelmistä keksintö eroaa nimenomaan siinä, ettei sen tavoitteena ole vaaleuden nostaminen vaan opasiteetin kasvattaminen. Erityisesti on huomattava, että menetelmä eroaa tunnetuista valkaisukäsittelyistä myös siinä suhteessa, että käytetyt perhappoannokset ovat hyvin pieniä ja menettelyssä pyritään välttämään orgaanisen aineen liuottamista kuiduista.

Menetelmä ei ole varsinaisesti valkaisumenetelmä, eikä massan varsinaisessa valkaisussa käytetyillä kemikaaleilla ole minkäänlaista vaikutusta keksinnön toimivuuteen. Massa voi olla valkaistu ditioniitilla, peroksidilla, ditioniitilla ja peroksidilla tai olla jopa täysin valkaisematonta. Massan valmistuksessa käytetyillä kelatointi- tai muilla apuaineilla ei myöskään ole vaikutusta keksinnön toimivuuteen.



Massan sakeus perhapon lisäyskohdassa voi olla 1-40 %, lämpötila voi olla 20-100 °C. Massasulpun pH voi olla prosessista riippuen 3-11, edullisesti 4-8. Mikäli perhappo lisätään alkalisen peroksidivalkaisun joukkoon, on edullinen pH-alue kuitenkin 9-11. Sopiva reaktioaika perhapolla on 1-300 minuuttia prosessista riippuen.

Menetelmä soveltuu käytettäväksi mekaanisten massojen käsittelyyn, kuten hiokkeen (SGW, PGW) ja hierteen (TMP) tai kemimekaanisten massojen (CTMP) käsittelyyn. Massan valmistukseen käytetyllä puulajilla ei ole merkitystä keksinnön toimivuuden kannalta.

Sopivaksi perhappoannokseksi on havaittu 0,5-5 kg/massatonni, tyypillisesti 1-3 kg/massatonni. Käytettävä perhappo voi olla mikä tahansa veteen kohtuullisesti liukeneva perhappo. Edullisiksi on havaittu peretikkahappo ja perpropionihappo ja erityisen edullisiksi niiden tasapainoliuoksista valmistetut peroksidivapaat tisleet. Perhapon valmistustavalla ei ole vaikutusta keksinnön toimivuuteen. Perhappona voidaan käyttää joko tislaamalla tai muulla tavalla puhdistettuja perhappoliuoksia tai perhappojen tasapainoliuoksia. Myös erilaiset perhappojen seokset ovat käyttökelpoisia. Eräässä keksinnön muunnoksessa voidaan käyttää perhapon ja Caron hapon seosta.

#### Esimerkki 1

CTMP-massaa valkaistiin normaaliin tapaan peroksidilla. Valkaisuliuokseen lisättiin perhappoja, tulokset on esitetty taulukossa 1.

#### Taulukko 1

CTMP, valkaisuliuos: NaOH 24 kg + vesilasi 20 kg + H<sub>2</sub>O<sub>2</sub> 30 kg/tm 70 °C, sakeus 30 %, 120 min, kelatoitu massa, perhappo lisätty valkaisuun PAA = peretikkahappo, PPA = perpropionihappo

	Annos, kg/tm	Vaaleus, % ISO	Opasiteetti
Ei	-	78,4	64,9
PAA	2	79,1	67,2
PPA	2,2	78,3	70,7

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Tuloksista havaittiin, että perhapoilla saadaan aikaan selvästi korkeampi opasiteetti samalla vaaleustasolla kuin pelkallä peroksidivalkaisulla.



#### Esimerkki 2

Valkaistua CTMP-massaa käsiteltiin perhapoilla, tulokset on esitetty taulukossa 2.

#### Taulukko 1

Valkaistu CTMP

5 Jälkikäsittely

t = 50 °C, 30 min, pH 7, sakeus 5 %

	Annos, kg/tm	Vaaleus, % ISO	Opasiteetti
Ei	-	65,9	71,5
PAA	2	66,6	74,1
PPA	2,2	65,8	74,3

Tuloksista voidaan havaita, että jälkikäsittelyllä on selvä vaikutus opasiteettiin.

#### Esimerkki 3

Tehtaalta otettua ns. konemassaa, joka sisälsi 16 % havusellua, 64 % TMP-massaa ja 20 % päällystettyä hylkyä (perusmassaseos havu: TMP 20:80) käsiteltiin peretikkahapolla. Havusellu oli normaalia ECF-sulfaattimassaa. TMP oli valkaistu ditioniitilla. Tulokset on esitetty taulukossa 3.

#### Taulukko 3

Massaseos:

Konemassa

Havusellu

16 %

TMP Päällystetty hylky 64 % 20 %

		stetty Hylky	20 /	<u> </u>						
	30 min, 70 °C, Cs 3.2 % (koe tehty tehtaan vedellä)									
n:o	PAA, kg/tm	рН	TOC, kg/tm	Vaaleus, %ISO	Opasiteetti, %	Huom !				
0	0	5,0	10,4	71,9	91,3	Käsittelemätön				
1	Ŏ	4,9	9,6	71,6	91,8	30 min, 70 °C:ssa				
2	1	4,6	8,9	71,7	96,5	Tislattu PAA				
3	2	4,6	9,6	71,9	95,8	Tislattu PAA				
4	4	4,2	10,2	71,3	96,9	Tislattu PAA				
5	2	4,5	11,0	70,7	97,1	Tasapainoliuos				
6	1	5,0	9,5	71,6	93,7	Tislattu PAA				
7	2	4,9	10,3	71,5	94,4	Tislattu PAA				
8	2	5,0	10,1	68,8	93,4	Tasapainoliuos				

Tislattu PAA = 38 % PAA, 1 % H<sub>2</sub>O<sub>2</sub>

Tasapainoliuos = PAA 13 %, etikkahappo 22 %, H<sub>2</sub>O<sub>2</sub> 15 %

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Tuloksista havaitaan, että opasiteetti kasvoi huomattavasti PAA-käsittelyn ansiosta. Havaitaan myös, että tasapainoliuos vaikuttaa haitallisesti vaaleuteen. TOC-arvot (total organic carbon) osoittavat, ettei käsittely liuottanut merkittäviä määriä orgaanista ainetta kuiduista.



#### **Patenttivaatimukset**

- 1. Menetelmä mekaanisen massan käsittelemiseksi, tunnettu siitä, että massaan lisätään opasiteettiin vaikuttavana aineena alifaattista perkarboksyylihappoa määrässä 0,5-5 kg/massatonni.
- 5 2. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että alifaattista perkarboksyylihappoa lisätään määrässä 1-3 kg/massatonni.
  - 3. Patenttivaatimuksen 1 tai 2 mukainen menetelmä, tunnettu siitä, että alifaattinen perkarboksyylihappo on valittu joukosta permuurahais-, peretikka- tai perpropionihappo.
- 4. Jonkin edellisen patenttivaatimuksen mukainen menetelmä, tunnettu siitä, että alifaattinen perkarboksyylihappo on tislattu tai tasapainotettu peretikkahappo.
  - 5. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että alifaattinen perkarboksyylihappo lisätään massaan valkaisun yhteydessä tai sen jälkeen.
- 6. Patenttivaatimuksen 5 mukainen menetelmä, tunnettu siitä, että massa on val-15 kaistu vetyperoksidilla ja/tai ditioniitilla.
  - 7. Patenttivaatimuksen 1 tai 5 mukainen menetelmä, tunnettu siitä, että alifaattinen perkarboksyylihappo lisätään tyypillisesti massan sakeudessa 1-40 %.
  - 8. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että massaan lisätään alifaattisen perkarboksyylihapon ja Caron hapon seosta.
- Alifaattisen perkarboksyylihapon käyttö mekaanisen massan opasiteetin parantamiseksi, jolloin alifaattista perkarboksyylihappoa käytetään määrässä 0,5-5 kg/massatonni.
  - 10. Paperi, tunnettu siitä, että se on valmistettu patenttivaatimuksen 1 mukaisesti käsitellystä massasta.

## (57) Tiivistelmä

Keksintö kohdistuu menetelmään mekaanisen massan käsittelemiseksi siten, että massaan lisätään opasiteettiin vaikuttavana aineena alifaattista perkarboksyylihappoa määrässä 0,5-5 kg/massatonni.

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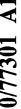
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(54) Title: METHOD TO IMPROVE THE OPACITY OF MECHANICAL PULP BY USING ALIPHATIC PEROXYACIDS AND USE OF PEROXYACIDS TO IMPROVE OPACITY

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PCT/FI00/00532

Method to improve the opacity of mechanical pulp by using aliphatic peroxyacids and use of peroxyacids to improve opacity.

The invention relates to a process for treating mechanical pulps, which can be used to affect the opacity of the pulp.

The nontransparent aspect of paper is described by opacity, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps (refiner mechanical pulp, groundwood pulp, and chemimechanical pulp) are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide bleaching.

It is well known that peracetic acid can be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before adding it to the pulp, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching solution (NaOH +  $H_2O_2$  + waterglass), it would readily cause silicate precipitate and consume the lye.

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Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP application 284598).

5 However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

The agent that affects the opacity of a technically useful pulp should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the bleaching. Because of environmental matters, a nitrogen-free substance would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, a substance should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

The purpose of this invention is to find a useful substance that is used in pulp bleaching and that affects the opacity, fulfilling the conditions mentioned above.

The main features of the invention are disclosed by the appended Claims.

Surprisingly, we have now observed that, when a small portion of peracid is either added to the peroxide bleaching or with the purpose of finishing the peroxide bleaching, the opacity of pulp improves compared with pulp of a corresponding brightness level that is bleached with hydrogen peroxide alone. At the same time, we have observed that peracids scarcely increase the brightness.

The use of peracetic acid in bleaching chemical pulps is disclosed by the published
Japanese application JP 57-21591, for example. However, bleaching processes like
this aim at removing the lignin from the pulp and, in this case, the purpose is in no
way to adjust the opacity of the pulp.

Tappi publication, Vol. 48, No. 2 (2/1965), W.H. Rapson et al. Paper Bleaching – A New Process, pp. 65-72, discloses a method for bleaching paper by using peracetic acid, among others. However, this method does not aim at improving the opacity of pulp, but increasing the brightness. Furthermore, the disclosed method uses considerable amounts of peracetic acid, about 1.2 – 2.5% (i.e., 12-25kg/ton of pulp). Such a portion can dissolve a considerable amount of lignin etc. from the pulp, whereupon the paper manufacturing process can be severely disturbed. The publication also reveals that the technical performance of the method deviates from our invention.

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The use of peracids as a biocide is also disclosed by publication Kemia, No. 3 (1995), Jyri Maunuksela, Mikrobien torjunta peretikkahapolla (Microbe Prevention with Peracetic Acid), pp. 242-244. Such a method aims at destroying microbe populations in the paper machine only. It is self-evident that peracetic acid, which is known to be an effective biocide, prevents the functioning of microbes in the water circulation, if a sufficient amount is present. The method disclosed by the publication uses a so-called equilibrium peracetic acid that contains a considerable amount of free acetic acid and hydrogen peroxide. The acetic acid and hydrogen peroxide that come with the peracid can disturb the paper manufacturing process.

Bleaching methods based on peracetic acid have also been presented, aiming at improving the brightness of the pulp compared with normal bleaching methods. Such a method is presented, for example, by publication Pulp and Paper Magazine of Canada, Convention Issue, 1972, pp. 123-131, and by number 3/1968 of the same magazine in pages 51-60. The doses of peracid used by these methods are very high and, consequently, dissolve a considerable amount of lignin from the surfaces of the fibres. In addition, these methods aim at increasing the brightness of the pulp, i.e. at bleaching.

One difference between the treatments mentioned above and our invention in particular is that the peracid treatments implemented by the means disclosed by them fail to improve the opacity of the pulp; none of the publications mentioned above tried to achieve a considerable increase in the opacity either.

The invention relates to a method, in which the peracid is either added to the peroxide bleaching or, preferably, after the peroxide bleaching, either to the storage tower of the bleached pulp or, for example, among the machine pulp in the paper machine. Typically, the amount of peracid added to the pulp is about 1-3 kg/ton of pulp. Because of its small amount, the peracid does not dissolve the lignin or the like from the pulp, whereupon it does not disturb the paper manufacturing process. It is especially advantageous to use peracid solutions, which have been purified, so that they mainly contain the peracid in question and water only. In that case, the addition of peracid does not have a considerable effect on the pH value of the stock, and no extra COD gets into the process. The invention differs from the known methods based on peracid namely in that it does not aim at increasing the brightness but growing the opacity. A matter worth noticing in particular is that the method differs from the known bleaching treatments also in that the peracid doses used are very small and the method tries to avoid the dissolution of organic matter from the fibres.

The method is not actually a bleaching method, and the chemicals used in the actual bleaching of the pulp have no effect whatsoever on the functioning of the invention.

The pulp can be bleached with dithionite, peroxide, dithionite and peroxide, or it can even be completely unbleached. Any chelation agents or other additives used in pulp manufacture have no effect on the functioning of the invention either.

The consistency of the pulp at the moment the peracid is added can be 1-40%; the temperature can be 20-100°C. Depending on the process, the pH of the stock can be 3-11, preferably 4-8. If the peracid is added to alkaline peroxide bleaching, an advantageous pH value is 9-11, however. A suitable reaction time for the peracid is 1-300 minutes depending on the process.

The method is well suited to the treatment of mechanical pulp, such as groundwood pulp (SGW, PGW) and refiner mechanical pulp (TMP), or to treat chemimechanical pulps (CTMP). The sort of wood used to manufacture the pulp has no importance to the functioning of the invention.

A suitable dose of peracid has been found to be 0.5-5 kg/ton of pulp, typically 1-3 kg/ton of pulp. The peracid used can be any peracid that reasonably dissolves in water. We have noticed that peracetic acid and perpropionic acid are preferable peracids, and especially preferable are the peroxide-free distillates that are prepared from the equilibrium solutions of these. The manufacturing method of peracid has no effect on the functioning of the invention. Peracid solutions that are either purified by distillation or some other method, or the equilibrium solutions of peracids can be used as peracid. Various mixtures of peracids are also usable. One modification of the invention can use a mixture of peracid and Caro's acid.

#### Example 1

CTMP pulp was bleached with peroxide in a normal manner. Peracids were added to the bleaching solution, the results are shown in Table 1.

#### 25 **Table 1**

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CTMP, bleaching solution: NaOH 24 kg +waterglass 20 kg +  $H_2O_2$  30 kg/ton of pulp, 70°C, consistency 30%, 120 min, chelated pulp, peracid added to the bleaching, PAA = peracetic, PPA = perpropionic acid

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	78.4	64.9
PAA	2	79.1	67.2
PPA	2.2	78.3	70.7

The results show that, by using peracids, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone.

#### Example 2

Bleached CTMP pulp was treated with peracids, the results are shown in Table 2.

#### Table 1

Bleached CTMP

#### 5 After-treatment

t = 50°C, 30 min, pH 7, consistency 5%

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	65.9	71.5
PAA	2	66.6	74.1
PPA	2.2	65.8	74.3

The results show that an after-treatment has an obvious effect on the opacity.

#### Example 3

So-called machine pulp taken from the plant and containing 16% of softwood pulp, 64% of TMP pulp, and 20% of coated broke (the basic pulp mixture was softwood: TMP 20:80) was treated with peracetic acid. The softwood pulp was normal ECF sulphate pulp. The TMP had been bleached with dithionite. The results are shown in Table 3.

#### 15 **Table 3**

-	•		mixture			
D,		2	m	12	***	TO.
_			111		ш	

Machine pulp

Softwood pulp

16%

**TMP** 

64%

Coated broke

20%

30 mir	n, 70°C, Cs 3.2%	6, (the	test was conduc	ted by using th	he water of the	plant)
No.	PAA, kg/ton of pulp	pН	TOC, kg/ton of pulp	Brightness, % ISO	Opacity, %	Note!
0	0	5.0	10.4	71.9	91.3	Untreated
1	0	4.9	9.6	71.6	91.8	30 min, at 70°C
2	1	4.6	8.9	71.7	96.5	Distilled PAA
3	2	4.6	9.6	71.9	95.8	Distilled PAA
4	4	4.2	10.2	71.3	96.9	Distilled PAA
5	2	4.5	11.0	70.7	97.1	Equilibrium solution
6	1	5.0	9.5	71.6	93.7	Distilled PAA
7	2	4.9	10.3	71.5	94.4	Distilled PAA
8	2	5.0	10.1	68.8	93.4	Equilibrium solution

Distilled PAA = 38% of PAA, 1% of  $H_2O_2$ 

Equilibrium solution = PAA 13%, acetic acid 22%, H<sub>2</sub>O<sub>2</sub> 15%

The results show that the opacity grew considerably because of the treatment with PAA. They also show that the equilibrium solution has an adverse effect on the brightness. The TOC values (total organic carbon) show that the treatment did not dissolve considerable amounts of organic matter from the fibres.

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#### **Claims**

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- 1. A method for treating mechanical pulp, characterized in that an aliphatic percarboxylic acid is added to the pulp, in the amount of 0.5 5 kg/ton of pulp, to affect the opacity.
- 2. A method according to Claim 1, characterized in that the amount of aliphatic percarboxylic acid that is added is 1-3 kg/ton of pulp.
- 3. A method according to Claim 1 or 2, characterized in that the aliphatic percarboxylic acid is selected from among performic acid, peracetic acid or perpropionic acid.
- 4. A method according to any of the preceding Claims, characterized in that the aliphatic percarboxylic acid is distilled or equilibrated peracetic acid.
- 5. A method according to Claim 1, characterized in that the aliphatic percarboxylic acid is added to the pulp in connection with or after bleaching.
- 15 6. A method according to Claim 5, characterized in that the pulp has been bleached with hydrogen peroxide and/or dithionite.
  - 7. A method according to Claim 1 or 5, characterized in that the aliphatic percarboxylic acid is typically added at a pulp consistency of 1-40%.
- 8. A method according to Claim 1, characterized in that a mixture of aliphatic percarboxylic acid and Caro's acid is added to the pulp.
  - 9. The use of aliphatic percarboxylic acid to improve the opacity of mechanical pulp, in which the amount of percarboxylic acid is 0.5 5 kg/ton of pulp.
  - 10. Paper, characterized in being manufactured from pulp treated according to Claim 1.

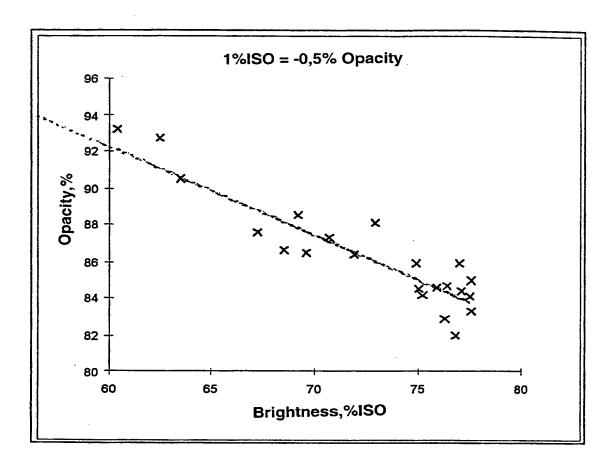


Fig. 1



#### INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00532

#### A. CLASSIFICATION OF SUBJECT MATTER IPC7: D21H 21/14 // D21H 17:14 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC7: D21H, D21C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched SE,DK,FI,NO classes as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Citation of document, with indication, where appropriate, of the relevant passages Category\* 1-10 US 5693185 A (HOU-MIN CHANG ET AL), X 2 December 1997 (02.12.97), column 1, line 61 - line 64, claims 1-5 WO 9722749 A1 (KVAERNER HYMAC INC.), 26 June 1997 1-10 X (26.06.97), see especially example 6, page 15, lines 10-12 and 31-34 GB 1119546 A (THE INSTITUTE OF PAPER CHEMISTRY), 1-8 X 10 July 1968 (10.07.68), see claim 1 9-10 A See patent family annex. Further documents are listed in the continuation of Box C. later document published after the international filing date or priority date and not in conflict with the application but cited to understand Special categories of cited documents: "A" document defining the general state of the art which is not considered the principle or theory underlying the invention to be of particular relevance "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive "E" erlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other step when the document is taken alone 'Y" document of particular relevance: the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than "&" document member of the same patent family the priority date claimed Date of mailing of the international search report Date of the actual completion of the international search 22 -09- 2000 15 Sept 2000 Authorized officer Name and mailing address of the ISA/ Swedish Patent Office Marie Karlsson/Els Box 5055, S-102 42 STOCKHOLM

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No. PCT/FI 00/00532

Patent document cited in search report			Publication date	P	atent family member(s)	Publication date
US	5693185	A	02/12/97	AU BR CA EP FI NO NZ US	672654 B 5347894 A 9307066 A 2141807 A 0660895 A 951334 A 951039 A 257205 A 5589032 A 9406964 A	10/10/96 12/04/94 13/10/99 31/03/94 05/07/95 21/03/95 17/03/95 28/10/96 31/12/96 31/03/94
WO	9722749	A1	26/06/97	AU	4271596 A	14/07/97
GB	1119546	A	10/07/68	DE FI JP	1692855 A 48366 B 54017041 B	21/10/71 31/05/74 27/06/79